

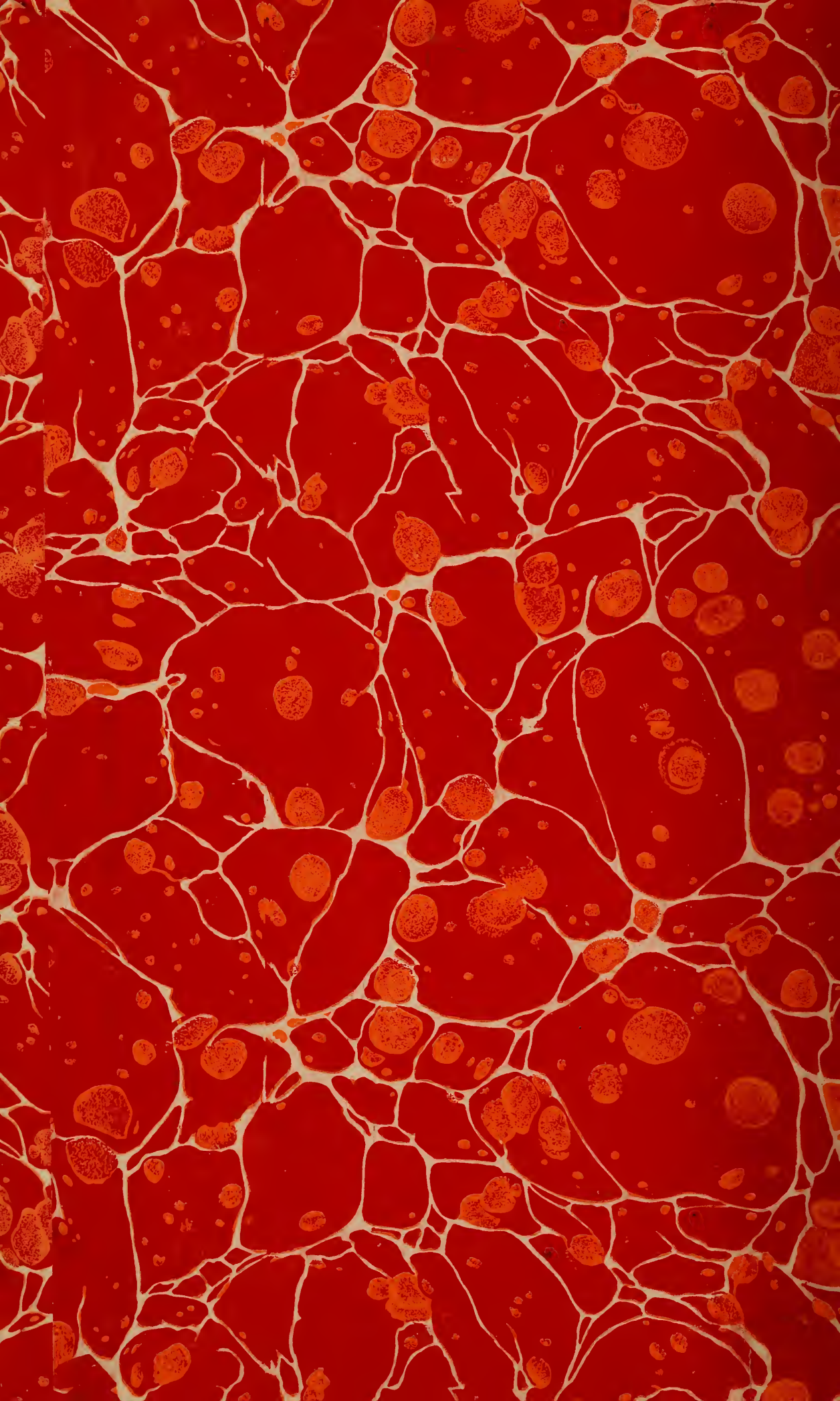
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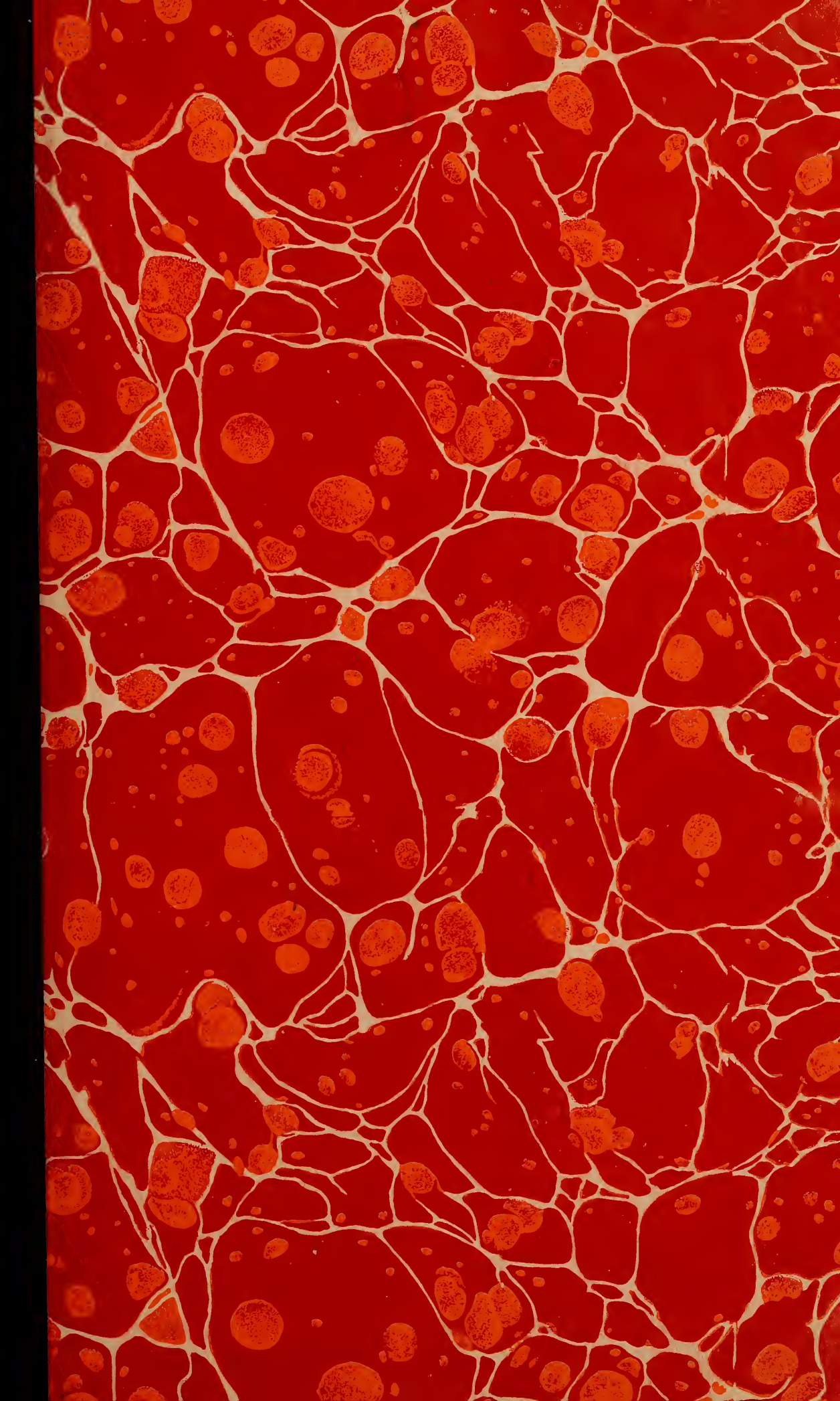
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THE HYDROLYSIS OF CHESTNUT AND QUEBRACHO TANNED LEATHERS BY SULPHURIC ACID

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ABSTRACT

Samples of leather tanned with chestnut and with quebracho extracts, to which sulphuric acid had been added, were hydrolyzed by heating with water at 60° C. for 18 hours and the total nitrogen in the solution determined. Similar samples of leather which had been aged were digested with water at room temperature (25° C.) and the total nitrogen in the solution determined. The degree of hydrolysis was found to be an approximate measure of the deterioration caused by sulphuric acid as determined by strength tests on new and aged samples of leather.

The results of the hydrolysis tests on both freshly prepared and aged leathers showed that quebracho-tanned leather was more resistant to deterioration by sulphuric acid than chestnut tanned leather.

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I. INTRODUCTION

It has been shown ¹ that leather deteriorates, as measured by the loss in strength, in the presence of sulphuric acid. The resistance of leather to deterioration has also been found to be greatly influenced by the tanning material used.¹ The results of 2-year aging tests on leathers tanned with (1) quebracho-wood extract, (2) chestnut-wood extract, and (3) a blend of the two extracts, treated with sulphuric acid, are shown in Figure 1. It was considered that a chemical study of what occurred during the disintegration of these leathers might yield information which would assist in explaining their behavior in the presence of sulphuric acid and in establishing a method for evaluation of leather.

The chief constituent of animal skin is collagen, a complex protein containing approximately 18 per cent of nitrogen. Collagen can be hydrolyzed by warm water and dilute acid solutions into decomposition products consisting of less complex proteins and amino acids.

Bowker, R. C., The Deterioration of Chestnut and Quebracho Tanned Leathers by Sulphuric Acid. J. Am. Lea. Chem. Assoc. 26. pp. 444-461; 1931.

Leather, a combination of animal skin and tanning materials, is more resistant to hydrolysis than collagen, is nonputrescible, and, when wet, will dry and retain its flexibility.

Vegetable-tanned leather can be hydrolyzed in boiling water. This method was used by W. Fahrion² and others for studying the hide-tanning combination. It was considered that any hydrolysis, re-

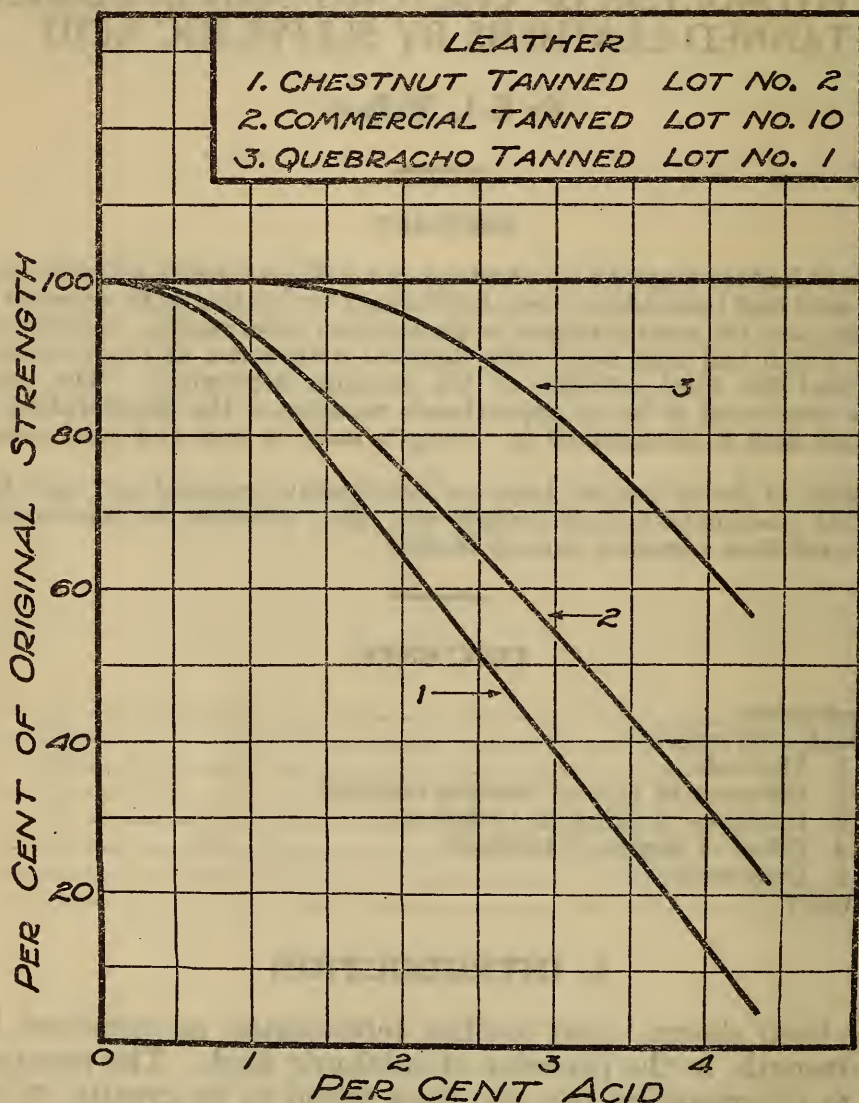


FIGURE 1.—Results of 24 months' aging tests on chestnut leather (lot 2), quebracho leather (lot 1), and commercial leather (lot 10), treated with sulphuric acid

Degree of tannage 62, 48, and 71, respectively.

sulting from the presence of sulphuric acid, might be measured in terms of soluble nitrogen at a temperature lower than that at which the hide substance would disintegrate.

Accordingly, a study of the hydrolysis of vegetable-tanned leather by sulphuric acid has been made on both tanned hide powder and on tanned hide aged for different periods.

² Collegium No. 338-339, pp. 495-50; 1908.

II. METHODS AND RESULTS

1. METHODS

Preliminary experiments showed that the treatment of leather at the boiling temperature was too drastic. The hide-tanning compound disintegrated and made it impossible to determine satisfactorily the hydrolysis resulting from the presence of sulphuric acid. Experiments at temperatures of 50°, 60°, and 70° C. were made, and it was found that leather well tanned with any of the commonly used vegetable materials would show no hydrolysis of its hide substance when digested with water for 18 hours at 50° or 60° C., whereas some leathers partially decomposed at 70° C. The temperature of 60° C. was chosen because the difference in amounts of soluble nitrogen, resulting from a small change in concentration of acid, was greater at this temperature than at 50° C., and more accurate results could be obtained. The period of 18 hours for the duration of the hydrolysis tests was selected arbitrarily after a study had been made of the effect of time and acid concentration on the rate of hydrolysis of a sample of hide powder tanned with a 50-50 blend of chestnut and quebracho extracts. Samples of this leather, each containing 5 g of hide substance, were treated with 200 ml of sulphuric acid solution. These series of tests were made to study the influence of the acid concentration on hydrolysis, using 0.03 *N*, 0.04 *N*, and 0.05 *N* acid solutions. Samples containing 5 g hide substance were digested with 200 ml of the acid solution at 60° C., and a sample from each series was tested every 2 hours, up to 22 hours, for dissolved nitrogen. The results of these tests are shown in Figure 2. The rate of hydrolysis was found to be practically constant after 10 hours and it appears that any time between 10 and 22 hours might be chosen for comparative work. Eighteen hours was selected because of convenience in handling the laboratory work and because the differences in hydrolysis, as influenced by acid concentration, may possibly be measured with less error.

In the case of aged samples of leather which contained sulphuric acid, it was found that soluble nitrogen compounds could be extracted with water at room temperature (25° C.) although none could be extracted at this temperature from leather containing no acid or from leather tested immediately after sulphuric acid was added.

The general method involved a digestion of the leather, for 18 hours, in water if acid was already present in the leather, or in an acid solution if the leather contained no acid. The temperature used was 60° C. except for one series of tests on aged leathers which were digested at room temperature (25° C.).

The hydrolyzed protein in solution was determined as nitrogen by the Kjeldahl method after first cooling the solution to room temperature and filtering it through a dry filter.

2. INFLUENCE OF TYPE OF TANNING MATERIAL

Samples of hide powder were tanned separately with chestnut, quebracho, and a 50-50 blend of chestnut and quebracho extracts. They were then washed for 24 hours in running distilled water, dried at room temperature and analyzed to determine the degree of tannage. Samples having a degree of tannage of approximately 60 were hydro-

lyzed with solutions of sulphuric acid at 60° C. for 18 hours and the soluble nitrogen determined in the extracts. The results are shown in Figure 3.

Similar tests were made also on chestnut, quebracho, and commercial leathers which had degrees of tannage of 62, 48, and 71, respectively. These leathers were treated so as to contain varying amounts of sulphuric acid and had been aged for 18 months. The

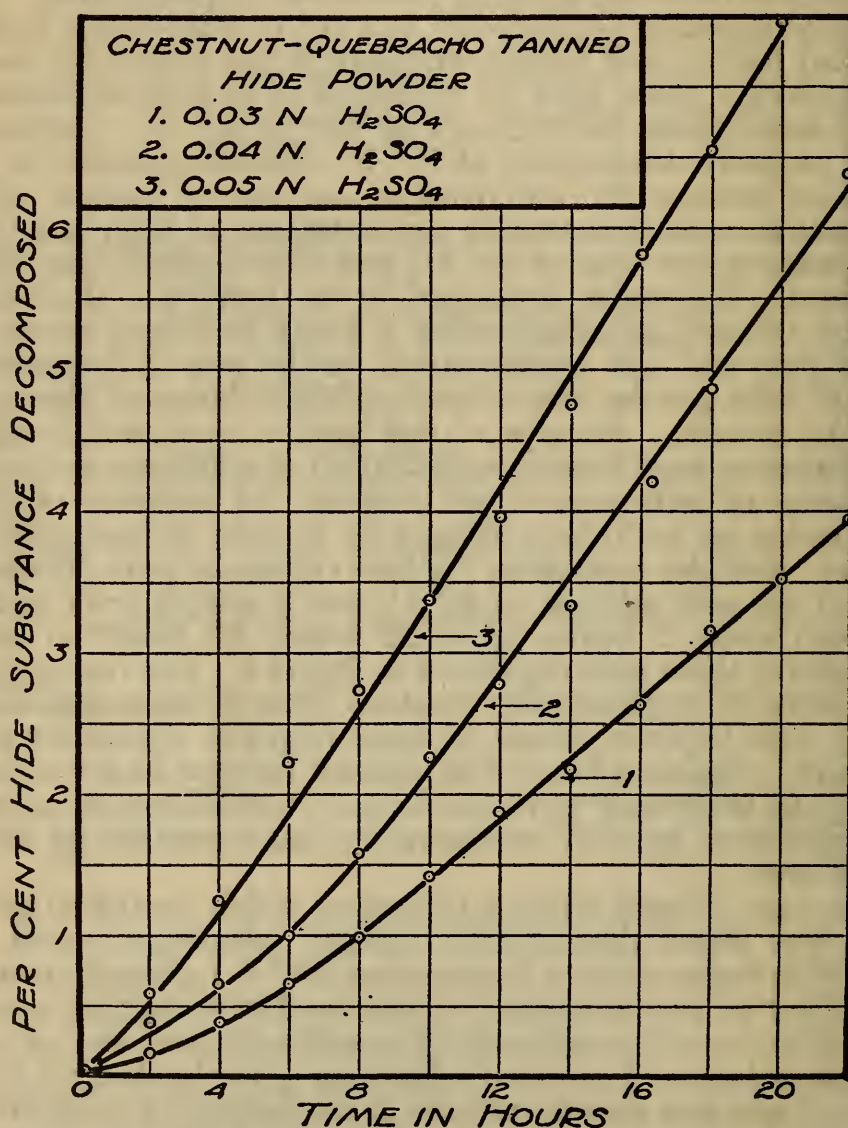


FIGURE 2.—The influence of time and acid concentration on the hydrolysis of hide powder tanned with a 50-50 blend of chestnut and quebracho extracts

Degree of tannage 54.

commercial leather was tanned with a blend made up chiefly of chestnut and quebracho extracts. Samples of these leathers were hydrolyzed with 200 ml of distilled water at 60° C. The results are shown in Figure 4.

These experiments, on both tanned hide powder and aged leather, showed that the kind of tanning material used greatly influenced the hydrolysis of hide substance by sulphuric acid.

3. INFLUENCE OF AGING ON HYDROLYSIS

Samples of quebracho and chestnut tanned leathers containing 5 g actual hide substance were extracted with 200 ml distilled water at room temperature (25° C.) by shaking for 18 hours, immediately after they had been treated with sulphuric acid and dried. The solution was filtered and soluble nitrogen determined. Other samples from the same blocks of leather were given a similar extrac-

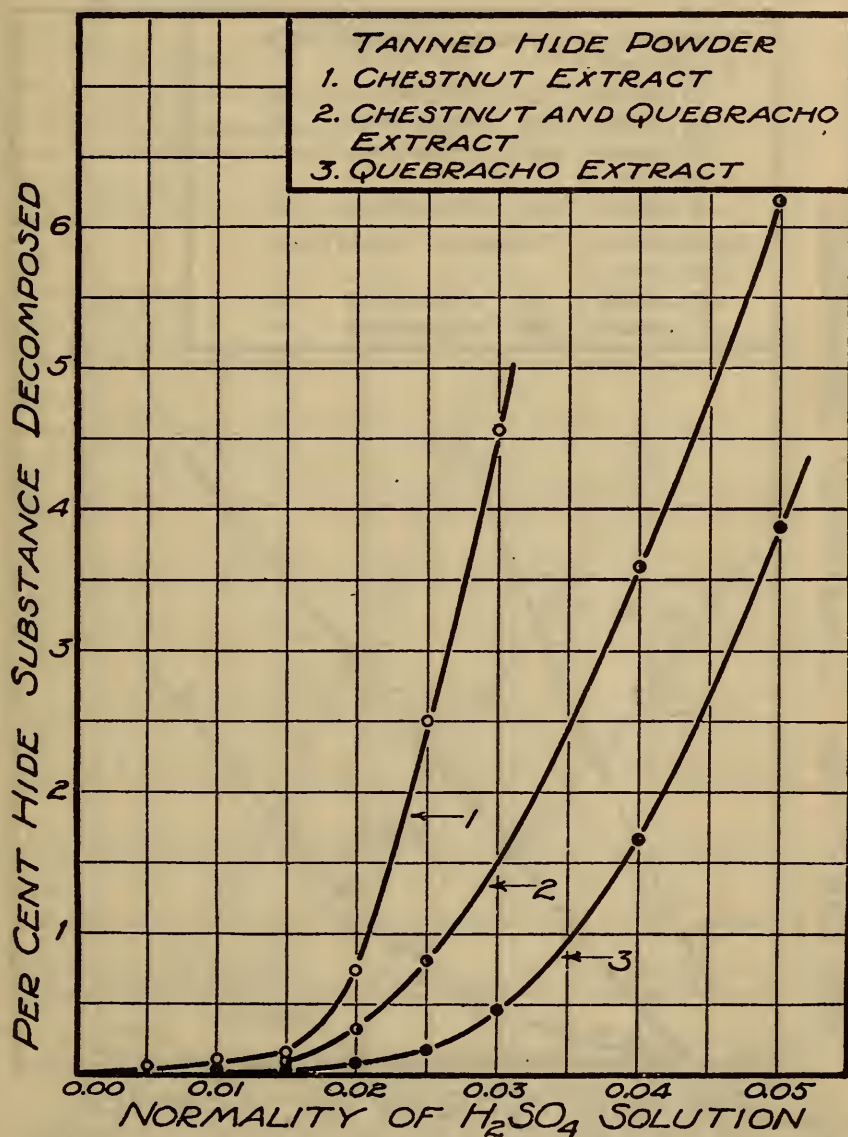


FIGURE 3.—The hydrolysis of tanned hide powder, degree of tan- nage 60, as influenced by acid concentration and the type of tanning material used

tion after aging for periods of 24 and 36 months. The results (fig. 5) show the relation between acid content, aging, and water soluble nitrogen compounds.

No hydrolysis occurred in the samples tested immediately after treatment with acid, but as aging progressed hydrolysis increased as illustrated by the results on the quebracho leather (curves 1, 2, and 3, fig. 5) and on the chestnut leather (curves 5 and 6).

4. EFFECT OF DEGREE OF TANNAGE

Samples of hide powder were tanned with different amounts of chestnut extract, quebracho extract, and a 50-50 blend of chestnut and quebracho extracts. The tanned hide powder was washed with distilled water until the wash water was free from tannin, as determined by the gelatine salt test, dried at room temperature, and analyzed to determine the degree of tannage. Samples containing 5 g of

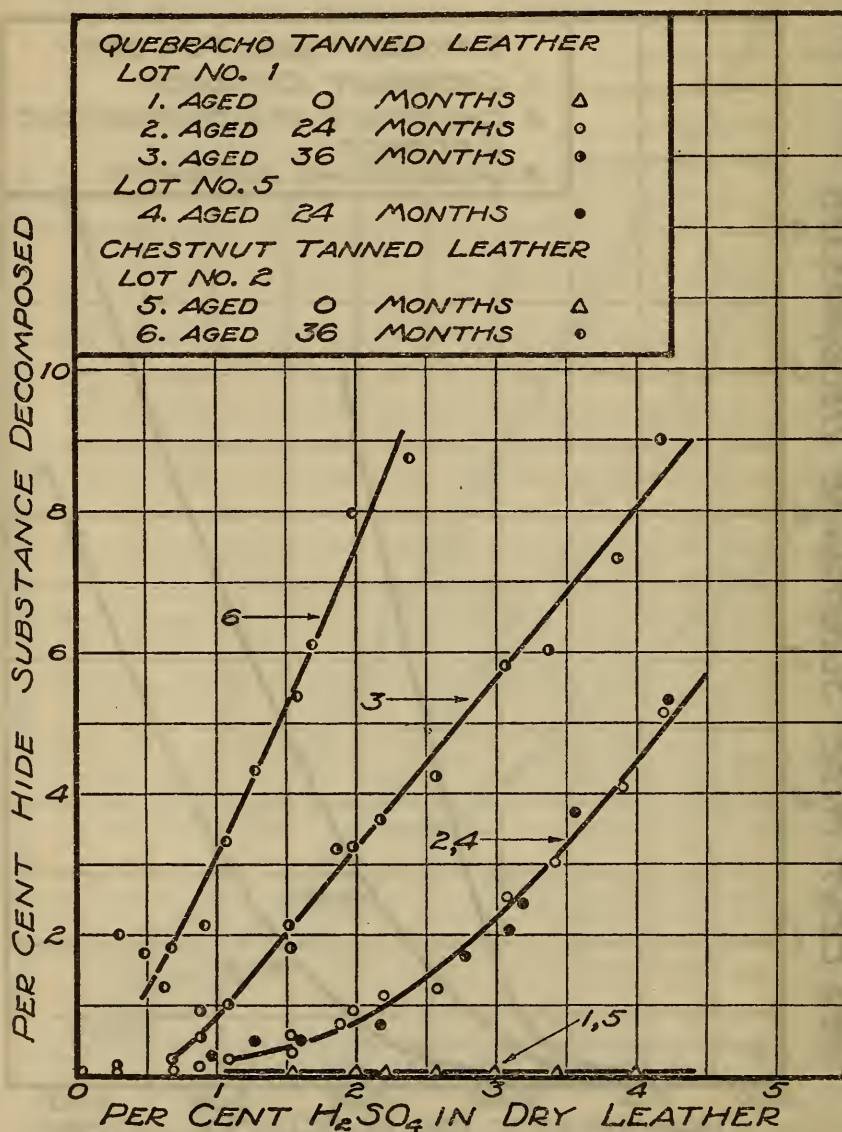


FIGURE 4.—Results of hydrolysis tests on chestnut leather (lot 2), quebracho leather (lot 1), and commercial leather (lot 10), aged for 18 months

Degree of tannage 62, 48, and 71, respectively.

hide substance were then hydrolyzed with 200 ml of 0.005 *N* sulphuric acid solution at 60° C. for 18 hours and the amount of soluble nitrogen per 5 g of hide substance determined. The results (fig. 6) show that there was less hydrolysis with the same quantity of acid as the degree of tannage was increased, and that more hide substance was hydrolyzed, at the same degree of tannage, for the samples tanned with chestnut extract than for those tanned with quebracho extract.

5. DISCUSSION

This investigation indicates that the disintegration of vegetable-tanned leather by sulphuric acid is accompanied by the formation of decomposition products which can be extracted from the leather, under certain arbitrary conditions, as soluble nitrogen compounds. This method of measurement showed that, for any given leather, the hydrolysis was greater as the time of aging and acid concentrations

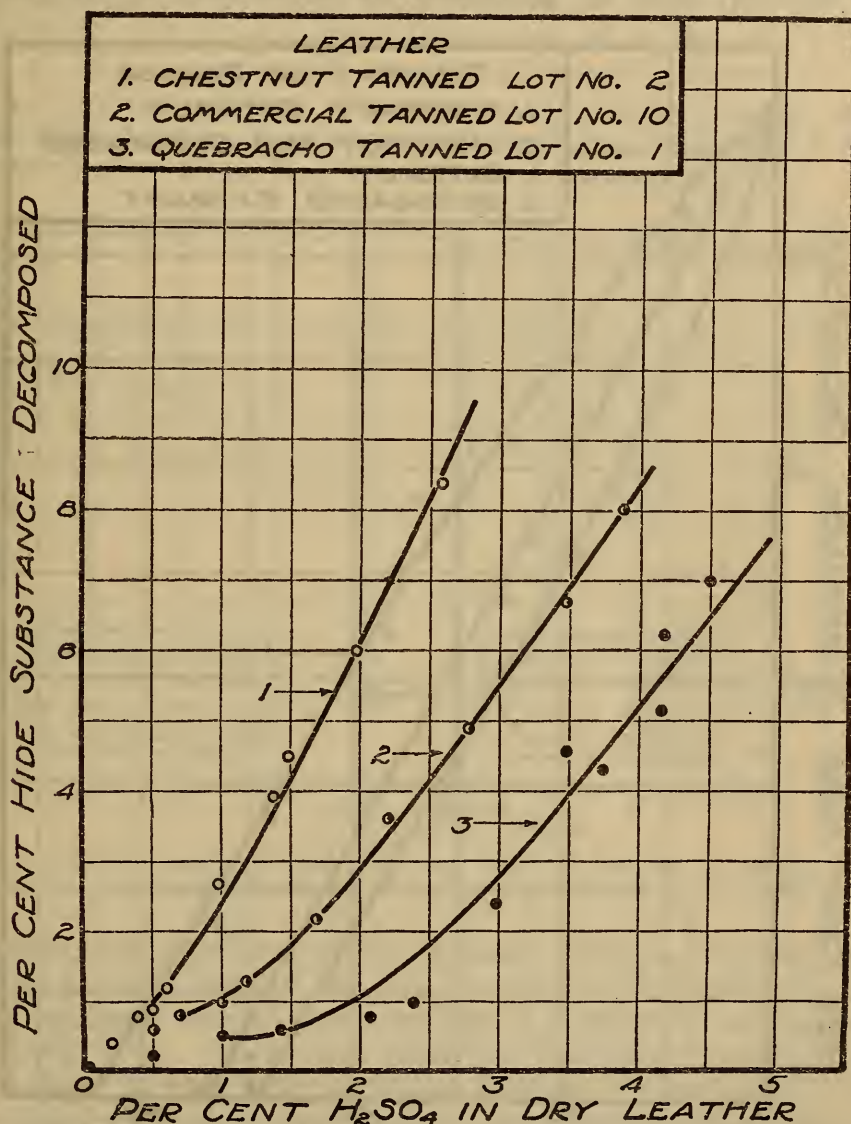


FIGURE 5.—The influence of time on the hydrolysis of aged leathers containing sulphuric acid

Lot 1, lot 2, and lot 5, having a degree of tannage of 48, 62, and 78, respectively.

present were increased. Similar results were secured whether leather containing acid was hydrolyzed with water or whether leather containing no added acid was hydrolyzed with acid solutions, as shown by the results in Figures 3 and 4.

The leather tanned with quebracho extract resisted hydrolysis better than the leather tanned with chestnut extract. It is significant that the hydrolysis results obtained on such leathers (fig. 4) closely parallel the deterioration of these leathers in actual aging tests as

measured by the drop in tensile strength. (Fig. 1.) There appears to be, for each leather, a limiting acid content below which deterioration proceeds at a low rate and above which it proceeds at a much greater rate as measured by both the hydrolysis and the loss of strength on aging.

This correlation of physical and chemical results indicates that the resistance to deterioration by sulphuric acid, of any vegetable-tanned leather, may be predicted by laboratory hydrolysis tests.

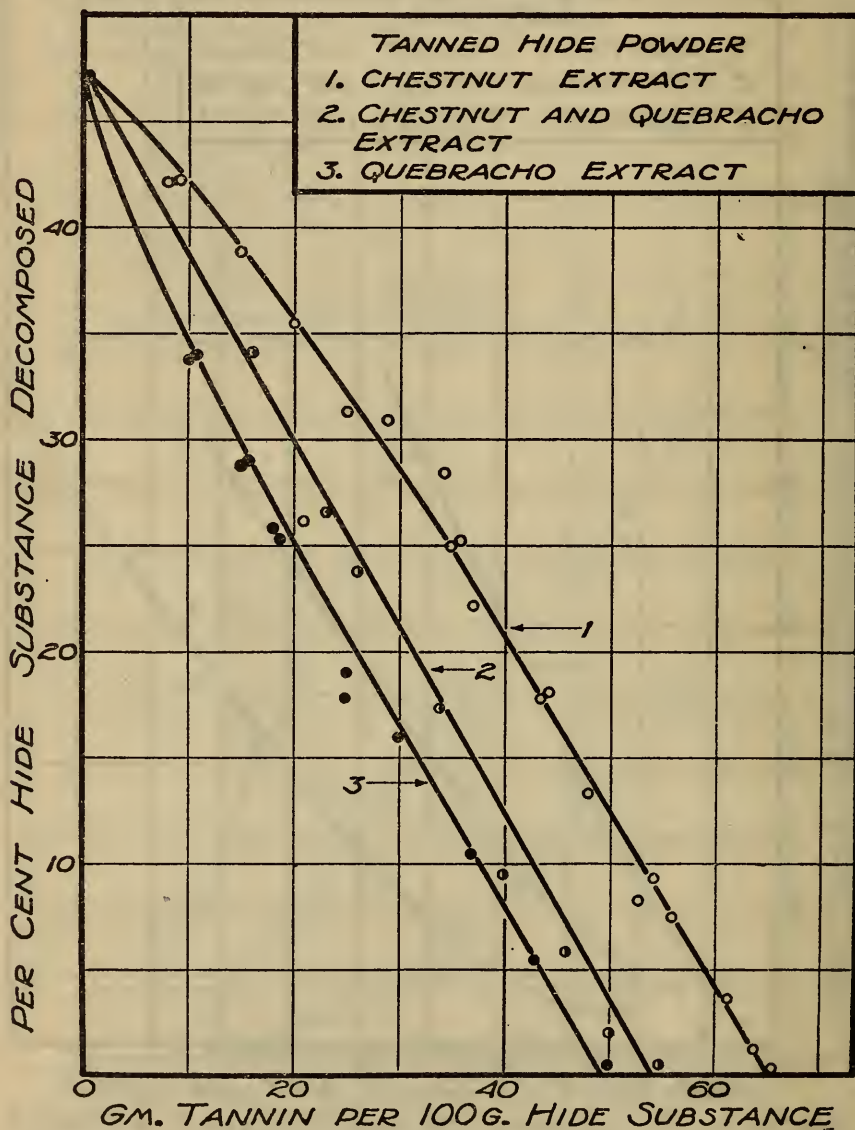


FIGURE 6.—The influence of degree of tannage on the hydrolysis of tanned hide powder when heated with 0.005 N H_2SO_4 at 60° C. for 18 hours

The method also suggests a possibility of being useful in determining the damage which may have already occurred in a sample of leather of unknown characteristics.

The studies of the influence of the degree of tannage on the hydrolysis of tanned hide powder definitely show (fig. 6) that hydrolysis, resulting from the action of a sulphuric acid solution on samples of leather for 18 hours at 60° C., decreased as the combined tannin increased.

From these results, in view of the parallelism between the hydrolysis tests (figs. 3 and 4) and the deterioration tests during aging (fig. 1) it might be expected that a high degree of tannage leather would show less deterioration and hydrolysis after aging than a low degree of tannage leather. However, this is not the case. Two quebracho leathers having degrees of tannage of 48 (lot No. 1) and 78 (lot No. 5) exhibited the same degree of hydrolysis after being aged for 24 months. (Curves 2 and 4, fig. 5.) The deterioration of these leathers as measured by the change in tensile strength and also of two chestnut leathers having degrees of tannage of 64 (lot No. 2) and 52 (lot No. 4), after aging for 24 months, is shown in Figure 7. These results are typical of those obtained at other aging periods and show that the high degree of tannage leathers have deteriorated slightly more than the corresponding low degree of tannage leathers.

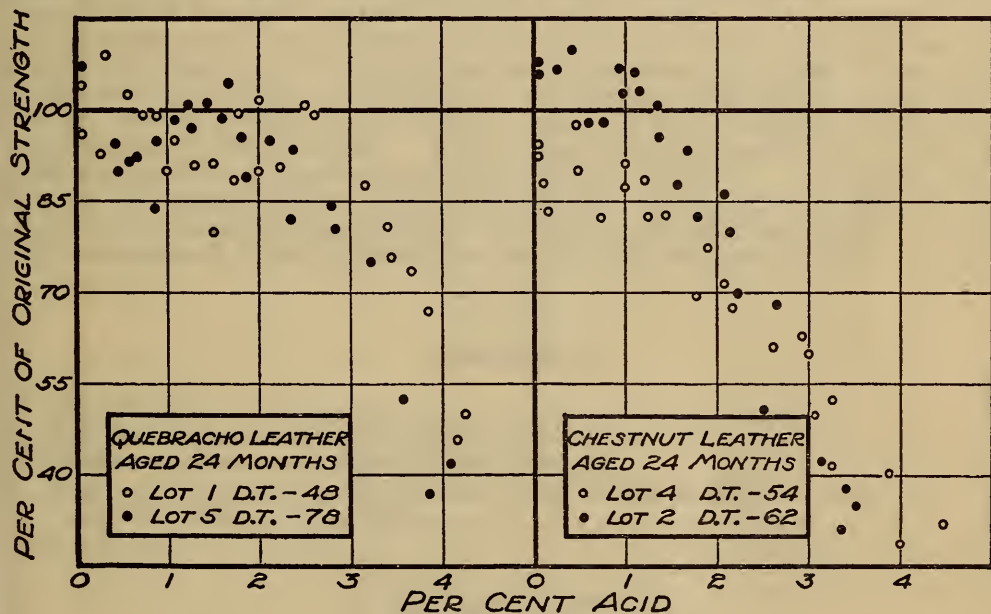


FIGURE 7.—Deterioration of quebracho and chestnut leathers by sulphuric acid as influenced by the degree of tannage

No explanation is offered of the apparent failure of hydrolysis tests on freshly tanned leather (fig. 6) to predict the influence of the degree of tannage on the deterioration of leather by sulphuric acid during aging tests. It appears that the indicated protective effect of the tannins is overcome by other factors, during aging tests to such an extent that a high degree of tannage leather will deteriorate at least as rapidly as a similar leather having a lower degree of tannage. Further studies of the mechanism of hydrolysis and the nature of the resulting decomposition products are in progress.

III. SUMMARY

The results for the hydrolysis of leathers examined by the methods used may be summarized as follows:

1. The disintegration of leather by sulphuric acid results in hydrolysis of the hide substance.

2. The hydrolyzed hide substance can be extracted from the leather as soluble nitrogen compounds.

3. Leather tanned with quebracho extract is more resistant to hydrolysis by sulphuric acid than leather tanned with chestnut extract.

4. The rate of hydrolysis of freshly tanned leather decreases as the degree of tannage increases.

WASHINGTON, June 26, 1931.



The following table shows the results of the hydrolysis of leather tanned with quebracho extract, as compared with leather tanned with chestnut extract. The results are expressed in terms of the percentage of nitrogen compounds extracted from the leather.

TABLE I

The results of the hydrolysis of leather tanned with quebracho extract, as compared with leather tanned with chestnut extract, are shown in the following table. The results are expressed in terms of the percentage of nitrogen compounds extracted from the leather.

